IMPROVED ALGORITHMS FOR CALCULATING SHEAR VISCOSITY IN IONIC LIQUIDS

C. J. F. SOLANO

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1. Theory

The *shear viscosity* η can be calculated using equilibrium fluctuations of the off-diagonal components ($\sigma_{\alpha\beta}$) of the *stress tensor*. For an isotropic system, the convergence of viscosity calculations can be improved by including equilibrium fluctuations of diagonal components of the stress tensor. In this case the generalized Green-Kubo formula is applied to the *symmetrized traceless portion* ($P_{\alpha\beta}$) *of the stress tensor* with appropriate weight factors for diagonal and off-diagonal elements:

$$\eta = \frac{V}{10k_BT}\sum_{\alpha}\sum_{\beta} q_{\alpha\beta}\int_0^{\infty}\langle P_{\alpha\beta}(t)P_{\alpha\beta}(0)\rangle dt, \tag{1}$$

where we sum over $\alpha, \beta = x, y, z$, V and T are volume and temperature of the system, k_B is the Boltzmann constant, $q_{\alpha\beta}$ is a weight factor ($q_{\alpha\beta} = 1$ if $\alpha \neq \beta$, $q_{\alpha\beta} = \frac{4}{3}$ if $\alpha = \beta$), and $P_{\alpha\beta}(t)$ is defined as

$$P_{\alpha\beta}(t) = \frac{\sigma_{\alpha\beta}(t) + \sigma_{\beta\alpha}(t)}{2} - \frac{\delta_{\alpha\beta}}{3}\sum_{\gamma}\sigma_{\gamma\gamma}(t), \tag{2}$$

where $\delta_{\alpha\beta}$ is the Kronecker delta and

$$\sigma_{\alpha\beta}(t) = \frac{1}{V}\left[\sum_{i}^{N} m_i v_{i\alpha}(t)v_{i\beta}(t) + \sum_{i>j}^{N} F_{ij\alpha}(t)r_{ij\beta}(t)\right] \tag{3}$$

being N total number of particles, $v_{i\alpha}$ α-component of the velocity of atom i, $F_{ij\alpha}$ α-component of the force exerted on atom i by atom j, and $r_{ij\beta}$ β-component of the vector $\vec{r}_{ij}$ separating atmos i and j .

Because $P_{\alpha\beta} = P_{\beta\alpha}$, Eq. 1 can be written as

$$\eta = \frac{V}{10k_BT}\left(\frac{4}{3}\sum_{\alpha}\int_0^{\infty}\langle P_{\alpha\alpha}(t)P_{\alpha\alpha}(0)\rangle dt + 2\sum_{\alpha}\sum_{\beta>\alpha}\int_0^{\infty}\langle P_{\alpha\beta}(t)P_{\alpha\beta}(0)\rangle dt\right). \tag{4}$$

According Einstein relations, integrals which appear in Eq. 4 can be described as

$$\int_0^{\infty}\langle P_{\alpha\beta}(t)P_{\alpha\beta}(0)\rangle dt = \lim_{t\to\infty}\frac{\langle[A_{\alpha\beta}(t) - A_{\alpha\beta}(0)]^2\rangle}{2t}, \tag{5}$$

where $\frac{dA_{\alpha\beta}(t)}{dt} = P_{\alpha\beta}(t)$. Using above equation, Eq. 4 can be written as

$$\eta = \lim_{t\to\infty}\eta(t), \tag{6}$$

where

$$\eta(t) = \frac{V}{10k_BTt}\left(\frac{2}{3}\sum_{\alpha}\langle[A_{\alpha\alpha}(t) - A_{\alpha\alpha}(0)]^2\rangle + \sum_{\alpha}\sum_{\beta>\alpha}\langle[A_{\alpha\beta}(t) - A_{\alpha\beta}(0)]^2\rangle\right). \tag{7}$$

Haile has shown that in a system with periodic boundary conditions the viscosity cannot be calculated using the conventional Einstein formula, which involves atomic coordinates and velocities. Because $\frac{dA_{\alpha\beta}(t)}{dt} = P_{\alpha\beta}(t)$, one can write following equation

$$\Delta A_{\alpha\beta}(t) = A_{\alpha\beta}(t) - A_{\alpha\beta}(0) = \int_0^t P_{\alpha\beta}(t')dt'. \tag{8}$$

Using above equation, Eq. 7 can be written as

$$\eta(t) = \frac{V}{10k_BTt}\left(\frac{2}{3}\sum_{\alpha}\langle[\Delta A_{\alpha\alpha}(t)]^2\rangle + \sum_{\alpha}\sum_{\beta>\alpha}\langle[\Delta A_{\alpha\beta}(t)]^2\rangle\right). \tag{9}$$

2. Implementation

In realizing Eq. 9 from simulation, the brackets would be interpreted as averages over *time origins*

$$\eta(t) = \frac{V}{10k_BTt}\left(\frac{2}{3}\sum_{\alpha}\lim_{\tau\to\infty}\frac{1}{\tau}\int_0^{\tau}\left[\Delta A_{\alpha\alpha}(t;t_0)\right]^2 dt_0 + \sum_{\alpha}\sum_{\beta>\alpha}\lim_{\tau\to\infty}\frac{1}{\tau}\int_0^{\tau}\left[\Delta A_{\alpha\beta}(t;t_0)\right]^2 dt_0\right), \tag{10}$$

where

$$\Delta A_{\alpha\beta}(t;t_0) = A_{\alpha\beta}(t+t_0) - A_{\alpha\beta}(t_0) = \int_{t_0}^{t_0+t} P_{\alpha\beta}(t')dt'. \tag{11}$$

In simulations, one uses discrete time steps, so that one has a set of discrete times $\{t_1, t_2, \ldots, t_{N_{tot}}\}$, where $t_i = t_0 + (i-1)\Delta t$ for $i = 1, 2, \ldots, N_{tot}$ and Δt is the *time step*. *Total time simulation* is given by $t_{simul} = t_{N_{tot}} - t_1$. Time origins

belong to set of discrete times $\{t_1, t_2, \ldots, t_{N_{or}}\}$, where $N_{or} = \frac{N_{tot}}{2}$. *Elapsed time* is set equal to $t = n\Delta t$, where $n = 1, 2, \ldots, N_{or}$. Thus, $\eta(t)$ (Eq. 10) can be obtained from

$$\eta(t) = \frac{V}{10k_BTn\Delta tN_{or}} \sum_{i=1}^{N_{or}} \left(\frac{2}{3} \sum_{\alpha} \left[\Delta A_{\alpha\alpha}(t;t_i)\right]^2 + \sum_{\alpha} \sum_{\beta>\alpha} \left[\Delta A_{\alpha\beta}(t;t_i)\right]^2 \right). \tag{12}$$

Because the integrand values are known at equally spaced steps and lower and upper limits are also known, trapezoidal and simpson's quadrature can, in principle, be useful for numerical integration of $\Delta A_{\alpha\beta}(t;t_i)$. Thereby, one can use an *extended trapezoidal rule* such that

$$\begin{aligned} \Delta A_{\alpha\beta}(t;t_i) &= \Delta t \left[\frac{1}{2} P_{\alpha\beta}(t_i) + P_{\alpha\beta}(t_i + \Delta t) + P_{\alpha\beta}(t_i + 2\Delta t) + \ldots \right. \\ &+ \left. P_{\alpha\beta}(t_i + (n-1)\Delta t) + \frac{1}{2} P_{\alpha\beta}(t_i + n\Delta t) \right], \end{aligned} \tag{13}$$

as well as an *extended Simpson's rule* such that

$$\begin{aligned} \Delta A_{\alpha\beta}(t;t_i) &= \Delta t \left[\frac{1}{3} P_{\alpha\beta}(t_i) + \frac{4}{3} P_{\alpha\beta}(t_i + \Delta t) + \frac{2}{3} P_{\alpha\beta}(t_i + 2\Delta t) + \frac{4}{3} P_{\alpha\beta}(t_i + 3\Delta t) + \ldots \right. \\ &+ \left. \frac{2}{3} P_{\alpha\beta}(t_i + (n-2)\Delta t) + \frac{4}{3} P_{\alpha\beta}(t_i + (n-1)\Delta t) + \frac{1}{3} P_{\alpha\beta}(t_i + n\Delta t) \right]. \end{aligned} \tag{14}$$

Both equations can be written in a simple way through

$$\Delta A_{\alpha\beta}(t;t_i) = \Delta t J_{\alpha\beta}(t;t_i), \tag{15}$$

where $J_{\alpha\beta}(t;t_i)$ is obtained directly from above equations. Using Eq. 15, Eq. 12 can be written as

$$\eta(t) = \frac{V\Delta t}{10k_BTnN_{or}} \sum_{i=1}^{N_{or}} \left\{ \frac{2}{3} \sum_{\alpha} \left[J_{\alpha\alpha}(t;t_i)\right]^2 + \sum_{\alpha} \sum_{\beta>\alpha} \left[J_{\alpha\beta}(t;t_i)\right]^2 \right\}. \tag{16}$$

3. Borodin's implementation

In previous section, we have described the correct expressions for calculating shear viscosity. However, an important modification has been included in Borodin's implementation for shear viscosity which is not theoretically justified. In what follows, we shall describe this modification. In turn, next section will describe numerical differences between Borodin's implementation and right implementation.

In Borodin's implementation, one replaces the symmetrized traceless portion of the stress tensor, $P_{\alpha\beta}(t)$, by dynamic quantity

$$\delta P_{\alpha\beta}(t) = P_{\alpha\beta}(t) - \langle P_{\alpha\beta} \rangle, \tag{17}$$

where

$$\langle P_{\alpha\beta}\rangle = \frac{1}{t_{simul}}\int_{t_1}^{t_{N_{tot}}} P_{\alpha\beta}(t)dt = \frac{1}{N_{tot}}\sum_{i=1}^{N_{tot}} P_{\alpha\beta}(t_i). \quad (18)$$

This modification changes a little bit some equations obtained in previous sections. Thus, one should be sustituted $P_{\alpha\beta}$ by $\delta P_{\alpha\beta}$ in Eqs. 1, 4, 5, 8, 11, 13 and 14. Notice that $\frac{dA_{\alpha\beta}(t)}{dt} = \delta P_{\alpha\beta}(t)$ for this modification.

4. Tests

I've implemented different code versions for shear viscosity algorithm which I describe below. Trapezoidal and Simpson's rules have been implemented for numerical integration. For trapezoidal rule, there three different versions: (i) a version which uses extended trapezoidal rule in the simplest way; (ii) a version which uses trapezoidal rule in a recurrence relation form; and (iii) a version which uses modified *qtrap* routine (see *Numerical Recipes in Fortran 77: The art of scientific computing*, page 131). This last version allow to estimate if integrals achieve the convergence for a desired fractional accuracy. For Simpson's rule, there are two different versions: (i) a version which uses extended Simpson's rule in the simplest way; and (ii) a version which uses modified qsimp routine (see *Numerical Recipes in Fortran 77: The art of scientific computing*, page 133). Again, this last version allow to estimate if integrals achieve the convergence for a desired fractional accuracy. Besides, note that there is not way to implemented a recurrence relation from Simpson's rules which includes all time origins. On other hand, I've included Borodin's implementation in code versions so that one can compare the results.

Table 1 shows results for *apparent* shear viscosity (Eq. 16) using exact and Borodin's implementations as well as trapezoidal and Simpson's quadratures for numerical integration. Although one should have long time simulation for obtaining shear viscosity and equilibration run has to be realised before production run, these results shows as there is a significant different between exact and Borodin's implementations. Notice that trapezoidal rule in a recurrence form generates same results as extended trapezoidal rule (the only difference is that recurrence form employs less CPU time). In turn, trapezoidal and Simpson's quadratures show similar results.

Tests about convergence of integrals using trapezoidal and Simpson's rules (Eqs. 13 and 14) have been carried out. To this end, I've employed modified *qtrap* and *qsimp* routines as indicated above. Moreover, I've designed an *intelligent* algorithm. In this algorithm, if an integral doesn't converge for a given elapsed time then this elapsed time is not taking into account and, automatically, next elapsed time is calculated. The result of these tests have been that none of elapsed times

TABLE 1. $0.50LiTFSI - 0.50PYR_{14}TFSI$. Canonical ensemble simulation. Time integration step of 10 fs for the stress tensor. Total time simulation of 100 ps. t is elapsed time (in ps). η_{trap} and $\eta_{trap,borodin}$ are *apparent shear* viscosity for exact and Borodin's implementations (in $Pa \times s$), respectively, using extended trapezoidal rule. η_{simp} is *apparent* shear viscosity (in $Pa \times s$) using extended Simpson's rule.

t	η_{trap}	$\eta_{trap,borodin}$	η_{simp}
10	0.63094E-04	0.88190E-04	0.64741E-04
20	0.77157E-04	0.13088E-03	0.79451E-04
30	0.78902E-04	0.16960E-03	0.81334E-04
40	0.72403E-04	0.19270E-03	0.74756E-04
50	0.64734E-04	0.21490E-03	0.67082E-04

can be considered because always there are some integrals which don't converge. Therereby, one should explain this phenomenon. As is indicated in D. Bedrov, and G . D. Smith, *J. Chem. Phys.*, **112**, 7203 (2000), some care must be taken in the integration of $P_{\alpha\beta}$ because the stress tensor exhibits strong oscillatory behavior (see Fig. 2 in this paper). Thus, two important considerations have to be taking into account before running simulations for obtaining shear viscosity. First, one has to used sampling frequency of stress tensor lower than the fastest oscillations. Second, large amounts of CPU time is requiered for shear viscosity calculations. Additionally, alternative numerical integration methods could be an interesting field in future for calculating integrals involved in shear viscosity.